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**THEORETICAL STUDIES OF GAS PHASE ELEMENTARY AND
CARBON NANOSTRUCTURE GROWTH REACTIONS**

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Final Report**

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Accomplishment Abstract:

The results of theoretical studies of gas phase elementary reactions and carbon nanostructure growth reactions are reported for Development and Application of Liouville-von Neumann Dynamics Method, Collaboration with the AFRL, Development of Global Reaction Route Mapping (GRRM) Strategy for Automatic Search of Potential Energy Surfaces and its Application to Photochemical Reactions, and QM/MD Simulations of Carbon Nanostructure Growth Reactions. The most important accomplishments are development of the GRRM strategy for automatic search of chemical reaction pathways and its applications. GRRM consists of two search methods. ADDF (anharmonic downward distortion following) and AFIR (artificial force induced reaction) methods, and allows automatic and unbiased determination of the critical structures, such as minima and transition states as well as minima of seam of crossing and conical intersection between two surfaces. The strategy has been applied to photodissociation reactions of ketene, methylamine, formic acid, methyl ethyl ketone, acetone and NO₃. For instance, for NO₃, a totally unknown photodissociation mechanism through 100% roaming on an excited state has been predicted and later confirmed experimentally.

Accomplishments:

A. Development and Application of Liouville-von Neumann Dynamics Method for Efficient Direct Dynamics Calculations.

Previously we developed a novel first principles molecular dynamics method, called LvNMD, based on the Liouville-von Neumann equation for density matrix propagation and the Magnus expansion of the time evolution operator. In this funding period, we applied this method using the scc-DFTB (self-consistent charge density functional tight-binding) method to growth and collisions of carbon nanostructures. In paper 18 (in the archived publication list at the end of the report) LvNMD method has been adapted on a GPU.

In paper 22 the collision-induced fusion reaction of two C₆₀'s. was studied with LvNMD. In agreement with experimental data, the highest probability of fusion was found for collisions with incident energy range of 120–140 eV. In this energy region, fusion occurs by way of the formation of hot, vibrationally excited peanut-shaped structures within 1 ps. These nanopeanuts further undergo relaxation to short carbon nanotubes and are cooling by evaporation of short carbon chains during the next 200 ps. The size of the fusion product after the evaporation agrees well with the average size of carbon clusters experimentally detected after collisions on the microsecond time scale. In paper 10 LvNMD studies of the initial phase of bulk C₂ condensation into carbon nanostructures are reported. The time-dependent quantum mechanical approach leads to faster formation of carbon nanostructures than analogous Born–Oppenheimer simulations. These findings suggest that the condensation of bulk carbon is nonadiabatic in nature, with the critical role of electronic stopping as in ion-irradiation of materials. In paper 9 an approach for performing real-time dynamics of electron transfer in a prototype redox reaction that occurs in reactive collisions between neutral and ionic fullerenes is discussed. The LvNMD show that the electron transfer occurs within 60 fs directly preceding the collision of the fullerenes, followed by structural changes and relaxation of electron charge. The consequences of real-time electron dynamics are fully elucidated for the far-from-equilibrium processes of collisions between neutral and multiply charged fullerenes.

B. Collaboration with the AFRL.

Collaboration with the Viggiano group at AFRL at Hanscom AFB continued during this funding period. In paper 20 proton affinity and fluoride affinity of nerve agent VX at all of its possible sites were calculated by high-level QM methods. The protonation leads to various unique structures, with H⁺ attached to oxygen, nitrogen, and sulfur atoms; among which the nitrogen site possesses the highest proton affinity of $-\Delta E \sim 251$ kcal/mol, suggesting that this is likely to be the major product. In addition some H₂, CH₄ dissociation as well as destruction channels have been found, among which the CH₄ + [Et-O-P(=O)(Me)-S-(CH₂)₂-N+(iPr)=CHMe] product and the destruction product forming Et-O-P(=O)(Me)-SMe + CH₂=N+(iPr)₂ are only 9 kcal/mol less stable than the most stable N-protonated product. For fluoridization, the S-P destruction channel to give Et-O-P(=O)(Me)(F) + [S-(CH₂)₂-N-(iPr)₂]- is energetically the most favorable, with a fluoride affinity of $-\Delta E \sim 44$ kcal. Various F⁻ ion-molecule complexes are also found, with the one having F⁻ interacting with two hydrogen atoms in different alkyl groups to be only 9 kcal/mol higher than the above destruction product. These results suggest VX behaves quite differently from surrogate systems. In paper 26 and 16, theoretical calculations provided spectroscopic data supporting experiments.

C. Development of Global Reaction Route Mapping (GRRM) Strategy for Automatic Search of Potential Energy Surfaces.

The largest accomplishment during this funding period is the development of Global Reaction Route Mapping (GRRM) strategy for automatic and unbiased exploration of potential energy surfaces for chemical reactions and its applications to a variety of photochemical reactions. Recent reviews of the strategy has been published as paper 5. The first method in GRRM strategy is the ADDF (anharmonic downward distortion following) method, originally developed by Ohno and Maeda for a single potential energy surface (PES). As illustrated in Fig. 1, the ADDF method starts with a minimum (EQ) on a PES and, using anharmonic downward distortion as the guide, walks up the PES to all the normal coordinate directions until TSs are reached; once a TS is found, it walks down along the intrinsic reaction coordinate (IRC) to reach a next minimum or a dissociation limit. From every new minimum new search is repeated. When the code cannot find any new minimum or TS, the search is terminated. We extended the applicability of the method to crossings of multiple PESs (paper 25) as well as to large complex reaction systems; with this extension we can find automatically and without guesses all minimum conical intersections (MECIs) between two PESs of the same spin as well as minimum energy seams of crossing (MESXs) between different spin states. The application of this extension will be discussed in the next section.

The second and more powerful method in the GRRM strategy is the AFIR (artificial force induced reaction) method (papers 23, 15, . In this method, as illustrated in Fig. 2, two molecules are pressed using artificial force acting on a particular pair of atoms between the two molecules. With an appropriate magnitude of the force, the potential curve for interaction becomes barrierless and can easily be optimized; the minimum and a wiggle on the PES with force are good starting points for further optimization of the true (without force) minimum and TS, respectively. When all relevant atom pairs are examined with all possible relative orientations, all possible pathways for reactions between the two molecules are considered to have been

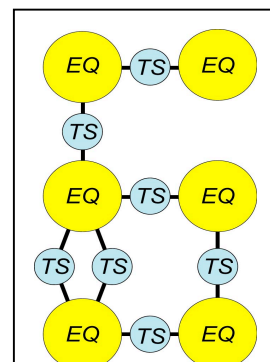


Fig. 1 Principle of the ADDF method

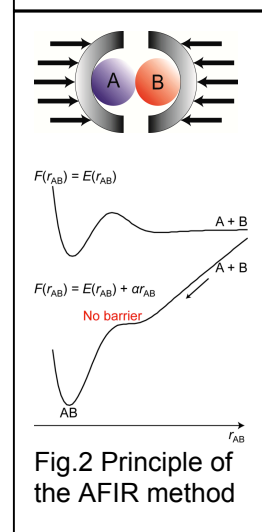


Fig.2 Principle of the AFIR method

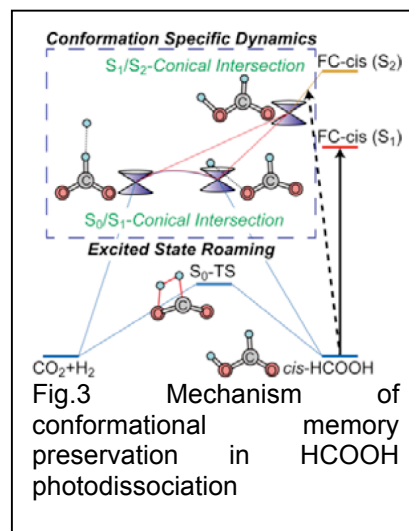
determined. This method is convenient for $A + B \rightarrow X$ type (addition) and its reverse (dissociation) reactions. The AFIR method has been extended to finding MECIs and MESXs. The AFIR method is substantially faster than ADDF or any other approach and has been applied to many reaction systems, including several catalytic reactions. The AFIR method has been applied to nonadiabatic ignition pathways of unsaturated hydrocarbons (paper 19). The method successfully found the best full catalytic pathway of the reaction of $\text{HCo}(\text{CO})_3$ catalyst with ethylene, carbon monoxide and H_2 (paper 12). The best pathway found out of ~90 intermediates and TS structures is the hydroformylation pathway, the experimentally established pathway. The important fact is that this pathway was found automatically without assumption of any order of reactions and in less than a week with two PCs! The AFIR method has been combined to the ONIOM hybrid method and is now applicable to large and complex molecular systems (paper 6). The AFIR method has recently been extended to reactions of excited state molecules (paper 2).

D. Application of GRRM Strategy to Photochemical Reactions.

The most impact-making applications of the GRRM strategy in connection to the present AFOSR project are for the nonadiabatic photodissociation mechanisms of small gas phase molecules. For such reactions MECIs and MESXs control the nonadiabatic processes; however it was very difficult to find these critical points manually. The GRRM strategy automatically finds these points with prejudice and therefore may totally unexpected MECIs and MESXs have been found and resulted in proposals of new reaction mechanisms.

The first successful applications were for carbonyl compounds. In the previous funding period, we found a new MESX between the lowest triplet and the ground state for formaldehyde, the molecule extensively be most modern experimentally techniques and high-level theoretical calculations for the last 30 years. The new pathway through this newly found MESX forced to change the long-accepted reaction pathway of photodissociation of formaldehyde. In acetaldehyde, in paper 24, structures of TSs as well as MESXs for PESs of acetone of the S_0 , S_1 , and T_1 states were explored. On the basis of the results, we propose a new mechanism, slow intersystem crossing from S_1 to T_1 without seam of crossing, followed by CH_3 dissociation via a TS on T_1 ; this slow pathway will be overtaken by a more efficient S_1 pathway for higher energy. This is consistent with the observed long lifetime of the S_1 species. Moreover, four channels, including three new ones, were found to regenerate the ground state acetone from the S_1 PES, and they all may be involved in the roaming channel that has been proposed recently as a new route of CO generation in a 230 nm photolysis. There are significant differences in MSX structures and energies between the present CASPT2 results and previous CASSCF results. For application to methyl ethyl ketone and an early review, see papers 21 and 13, respectively.

To elucidate the photodissociation mechanism of HCOOH , reaction pathways starting from the first excited singlet state (S_1) have been explored systematically by using automated reaction path search methods. All critical points, that is, minima, transition states, minimum energy conical intersections, and minima on seam of crossing, for the S_0 , T_1 , and S_1 PESs obtained in the present search were optimized at the CASPT2 level. The structure list obtained by the search explained all experimentally reported photolytic channels. A new mechanism for the previously suggested but unexplained conformational memory in the 193 nm photolysis is proposed, which involves two steps: partial dissociation and succeeding roaming of one of H atoms on the S_1 PES, followed by intramolecular recombination on the S_0 PES after



radiationless transition through a conical intersection at a partially dissociated geometry. The photodissociation mechanisms of ketene and methylamine have also been studied using the GRRM strategy in detail in paper 7 and 4.

The most impact-making work in photodissociation in the present funding period was the discovery of the “excited state 100% roaming” mechanism in NO₃ photodissociation. Roaming mechanisms have recently been observed in several chemical reactions alongside trajectories, in which an almost dissociated atom (or group) roams around the residual fragment and eventually extracts an atom to dissociate as a molecule, which takes place on the ground state PES and as a minor channel where direct path is the dominant channel. In paper 17 we predicted the first roaming dynamics that occurs as the exclusive (100%) channel and on an excited-state potential energy surface, not a minor channel on the ground state as in the previous examples. In the photodissociation of a nitrate radical, a systematic GRRM search at the CASPT2 level for nonadiabatic reaction pathways reaction path search showed that the photodissociation takes place on the first excited doublet D1 has a structure in which one O atom is nearly dissociated (Fig. 4). However,

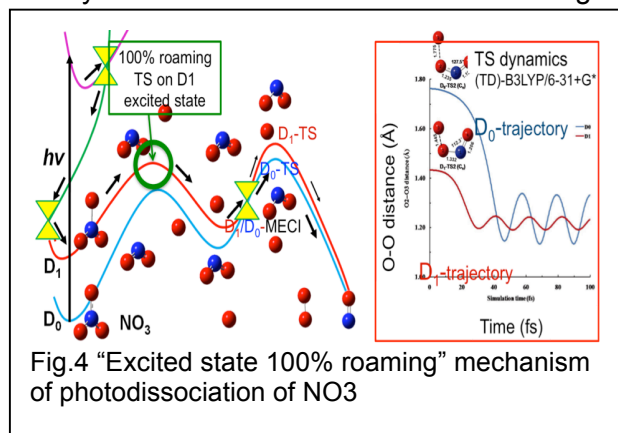


Fig.4 “Excited state 100% roaming” mechanism of photodissociation of NO₃

O cannot dissociate but roams around the remaining NO₂ group through the D1 minimum. The system can eventually reach to D1-TS. This TS leads to the dissociation product O₂ + NO with a large O₂ vibrational energy. Some of the trajectories roaming on D1 can cross to the D0 state via the low energy D1/D0-MECI. The D0 state can dissociate also to O₂ + NO, but the O₂ produced is low in vibrational energy. These findings explained recent experiments by North et al. Who found two distributions of O₂ vibrational excitation without being able to explain the origin of these two channels. Our work clearly explained two vibration distributions, assigning high vibrations to the D0 channel and low vibrations to the D1 channel. These predictions since then has been confirmed by a new experiment b North, resulting in a joint theoretical and experimental paper in Science (paper 11). Many D1 and D0 potential energy points have been calculated and fit to analytical functions in paper 7. Improved fits and classical MD calculations (paper 4) now explain experimental vibrational and rotational distributions quantitatively. Thus the new concepts of “100% roaming” and “excited state roaming” have been established.

E. QM/MD Simulations of Carbon Nanostructure Growth Reactions

We continued our quantum mechanical molecular dynamics (QM/MD) simulations of carbon nanostructure growth reactions. For technical reasons, most of the research along this line was performed using personal and computational resources in Japan.

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